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# Spectrophotometric Determination of Cobalt by Mineral Acid

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The absorption spectra were investigated for the solution of cobaltous perchlorate in mineral acid. It was found that the spectra were same in the cases of perchloric and sulfuric acid solution, but in hydrochloric acid solution bathochromic and hyperchromic effects were observed. A method for spectrophotometric determination of cobalt was studied by using the above acid as a reagent, and good results were obtained. The proposed method has low sensitivity but good accuracy and simplicity in the procedure. Beer's law was obeyed in the range of 0.05–0.3 *M*.

The spectrophotometric method for the determination of metal using mineral acid is convenient and useful, because no special color forming reagent is required.

In order to establish a series of the spectrophotometric determination of metallic ions, we have already published several works<sup>1-12)</sup>.

In the present paper the determination of cobalt using various acid such as hydrochloric, perchloric and sulfuric acid are studied. On the absorption spectra of cobaltous salt in solution there are many papers<sup>13-17)</sup>. Literature contains, however, few reports on the spectrophotometric determination of cobalt by the mineral acid method.

## APPARATUS AND MATERIALS

Spectrophotometric measurements were made with a Beckman Quartz Spectrophotometer, Model DU, with 1 cm transmission cells.

The stock solution of 0.500 *M* cobaltous perchlorate were prepared by the same procedures as in the case of nickel described previously.

## EXPERIMENTAL AND RESULTS

### Absorption Spectra

The absorption spectra of cobaltous perchlorate in various medium are shown in Fig. 1 and Table 1. The spectra in aqueous, sulfuric and perchloric acid solutions have shown no appreciable difference, but in hydrochloric acid solution bathochromic and hyperchromic effects are observed, and the absorption band at 510 *mμ* which may be due to aquo-ion, splitted to 523 and to 600–700 *mμ*. These effects show that the cobalt ion exists as aquo-ion in sulfuric or perchloric acid solution and in hydrochloric acid solution is converted to chloro-complex.

To investigate the effects of chloride and hydrogen ions, several spectra were

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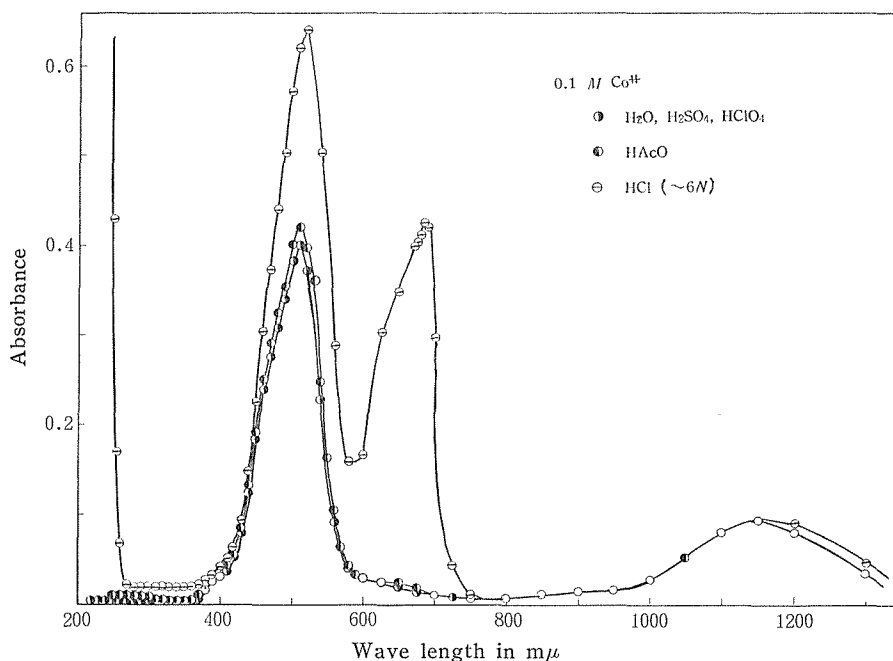


Fig. 1. Absorption curves of cobalt solutions.

Table 1. Absorption maxima of cobalt solution

Cobalt solution	Max. wave length in $m\mu$ (Molar extinction coeff.)		
$\text{Co}^{++}-\text{H}_2\text{O}$	510(3.90)		1145(0.96)
$\text{Co}^{++}-4.8\text{ N HClO}_4$	510(3.99)		1145(0.94)
$\text{Co}^{++}-6\text{ N HCl}$	518(6.42)	688(Ca. 5)*	1160(0.95)
$\text{Co}^{++}-6\text{ N H}_2\text{SO}_4$	510(3.99)		1145(0.95)
$\text{Co}^{++}-6\text{ N CH}_3\text{COOH}$	510(4.22)		1150(0.95)

\* Beer's law not obeyed.

determined at various constant acidity, as shown in Fig. 2 and 3. In the region of 600–700  $m\mu$  three splitted bands appeared and hyperchromic effect was observed as the increase of the chloride ion concentration.

The results on the absorption spectra in hydrochloric acid solution are summarized as follows.

1. The absorption band at 510  $m\mu$  shifts to longer wave lengths and also the absorbance increases as the acid concentration increases.

2. The absorption band at 685  $m\mu$  is observed when the acid concentration is more than 4–5 N and this band splits to three maxima (625, 660, 685  $m\mu$ ) with the increase of the acid concentration.

3. When the acidity is higher, a new band appears at 350  $m\mu$  with the increase of the chloride ion concentration but the absorbance decreases when the chloride

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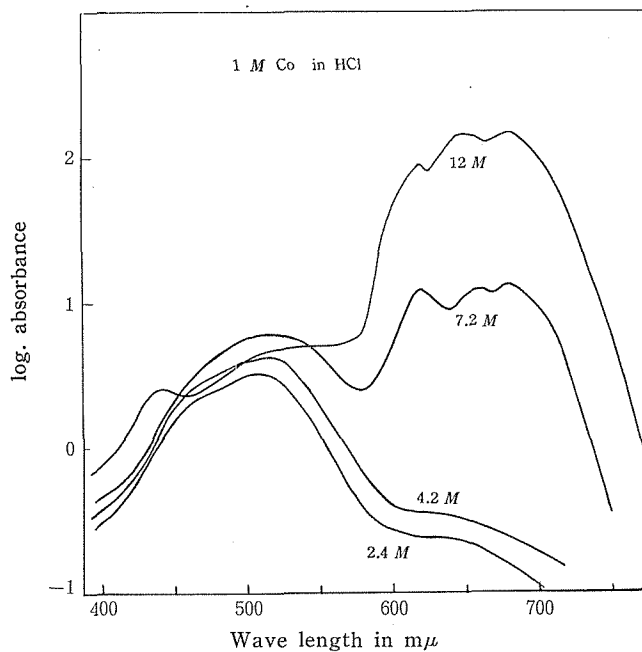


Fig. 2. Absorption curves of cobalt solutions.

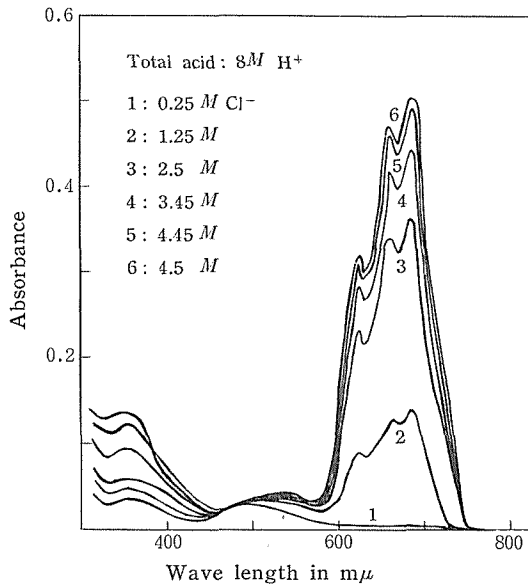


Fig. 3. Absorption curves of cobalt solutions.

ion concentration becomes greater than a certain value.

4. These effects may be attributed to the successive formation of chloro-complex, and this formation may be effected not only by the concentration of chloride ion but also by the hydrogen ion.

### Determination of Cobalt

From the above experiments, quite similarly to the case of nickel, there may be few difference when any of the acids, except hydrochloric acid, are used as the reagent. The calibration curves were made by using hydrochloric, perchloric and sulfuric acids, respectively, as shown in Fig. 4. In most cases, the Beer's law is obeyed. In the case of hydrochloric acid, it is necessary to keep the acid concentration constant, but in the other cases, such consideration is not required. In this experiment, the concentration of acids were held in 6.0 *N*, respectively.

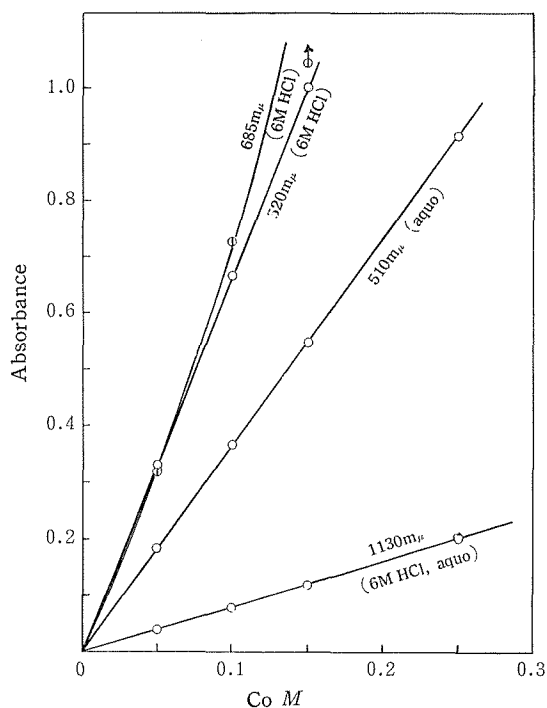


Fig. 4. Calibration curves for cobalt (aquo and chloro complex).

The application of these results to simultaneous determination of iron, cobalt and nickel will be reported shortly.

### SUMMARY

Spectrophotometric determination of cobalt using various acids such as hydrochloric, sulfuric and perchloric acid as the reagent were studied. The absorption spectra were determined in detail at various concentrations of the acids and it was found that the absorption spectra is quite similar in perchloric and sulfuric acid solutions, but in hydrochloric acid solution bathochromic and hyperchromic effects were observed as the increase of the concentration of the acid. The method of spectrophotometric determination of cobalt was then studied and good results were obtained. This method has the defect of low sensitivity but the merits of good accuracy and simplicity in the procedure. The method may be effectively applied

to the determination of the amounts of the metal in concentrated solution by a simple procedure.

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#### REFERENCES

- (1) M. Ishibashi, T. Shigematsu, Y. Yamamoto, M. Tabushi and T. Kitagawa, *J. Chem. Soc. Japan*, **76**, 758, (1955).
- (2) Idem, *Japan Analyst*, **5**, 280, (1956).
- (3) Idem, *Bull. Chem. Soc. Japan*, **29**, 57, (1957).
- (4) Idem, *ibid.*, **30**, 433, (1957).
- (5) M. Ishibashi, T. Shigematsu, Y. Yamamoto, M. Tabushi and M. Kitayama, *This Bulletin*, **35**, 6, (1957).
- (6) M. Ishibashi, Y. Yamamoto and K. Hiiro, *Japan Analyst*, **7**, 582 (1958).
- (7) Y. Yamamoto, *ibid.*, **8**, 513, (1959).
- (8) Y. Yamamoto, *This Bulletin*, **36**, 139 (1958).
- (9) Y. Yamamoto, *J. Chem. Soc., Japan*, **80**, 875, (1959).
- (10) Y. Yamamoto, *ibid.*, **80**, 1026 (1959).
- (11) Y. Yamamoto, *ibid.*, **80**, 1426 (1959).
- (12) M. Ishibashi, Y. Yamamoto and Y. Inoue, *This Bulletin*, **37**, 38, (1959).
- (13) A. Kiss, P. Csokan and M. Richter, *Acta Chem. Mineral Physk. Univ., Czeged*, **7**, 119, (1939).
- (14) L. Katzin and E. Gebert, *J. Am. Chem. Soc.*, **75**, 2830, (1953).
- (15) M. S. Barvinok, *Zhur. Fiz. Khim.*, **22**, 1100, (1948).
- (16) M. Bobtelsky and K. S. Spiegeler, *J. Chem. Soc.*, 1949, 143.
- (17) Y. Shibata, *J. Chem. Soc. Japan*, (Tokyo) **35**, 807, (1914).
- (18) T. Shigematsu, Y. Yamamoto, M. Tabushi and T. Kitagawa, *This Bulletin*, **38**, 307 (1960).